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Application of Laser Spectroscopy to Collisional Studies*

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I should like to thank the Comité d'Organisation for their kind invitation to participate in this Conference. I apologize for writing this summary of my talk in English rather than French, and ask the readers' indulgence on this point.

The traditional method for studying atomic or molecular collisions is the use of crossed atomic or molecular beams. Owing to the low beam densities one encounters, such studies have generally been restricted to atoms or molecules in ground or metastable states; however, it is now possible to use lasers to achieve substantial excited state atomic populations so that scattering from excited states may also be studied in crossed beam experiments. Typically, one obtains the differential scattering cross section as a function of center-of-mass energy in crossed beam experiments. These experiments, although often difficult to perform, provide a "direct" measure of the scattering process.

A somewhat less direct method for studying collisional processes in gases has been available for many years under the heading "pressure broadening." Since the absorptive properties of a vapor are affected by collisions occuring within the vapor, collisional information is implicitly contained in the absorption or emission profiles associated with various atomic transitions in the vapor. Using linear spectroscopy, one can measure the broadening (or narrowing) of the spectral profile associated with a given transition of "active" atoms as a function of perturber gas pressure. From such data, one can reach some conclusion regarding the total cross section for scattering between active atoms (in the states involved in the transition) and ground state perturbers. Using saturation spectroscopy or coherent transient techniques, one can also obtain information about *differential* scattering cross sections involving excited-state active atoms (see below), albeit of a somewhat different nature than that obtained in beam experiments.

Owing to time limitations, I shall not discuss linear spectroscopy,[2] and shall, instead, concentrate on the saturation spectroscopy of three-level systems. I shall also mention some coherent transient experiments that are particularly well-suited to collisional studies and a recent experiment employing a combination of atomic beam and laser spectroscopic techniques.

Before beginning to discuss three-level systems, it is perhaps useful to describe the type of collisional data one can

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hope to obtain from laser spectroscopic studies involving cells rather than beams. In a typical experiment, one uses a laser to excite active atoms having a specific longitudinal velocity and then probes the manner in which collisions with perturber atoms cause this velocity distribution to return towards equilibrium. Thus, in such an experiment, one measures the differential scattering cross section averaged over the perturber velocity distribution and the transverse active-atom velocity distribution. I have referred to this as a "poor man's" differential scattering cross section, since it contains less information than the corresponding cross sections obtained in beam experiments. Still, the "poor man's" differential cross section is rich enough to draw conclusions concerning the interatomic potential giving rise to the scattering. Moreover, the variety of cross-sections (elastic, inelastic, exchange, magnetic relaxation, etc.) that are easily probed using laser spectroscopic techniques guarantees, in my opinion, a promising future for this mode of collisional study.

Three-level Systems

Three-level systems have received considerable attention[3-18] for both high resolution and collisional studies. Figure 1 illustrates three types of three-level systems. The quantities β and β' label the different level schemes so that all may be treated by a single formalism; $\beta = \beta' = 1$ in Fig. 1a (upward cascade); $\beta = 1, \beta' = -1$ in Fig. 1b (inverse V); $\beta = -1$ $\beta' = 1$ in Fig. 1c (V). The three levels are incoherently pumped at some rate density $\lambda_i(v)$ ($i = 1,2,3$) and each level decays at some rate γ_i. External fields having frequency Ω and Ω' drive the 1 - 2 transition (frequency ω)

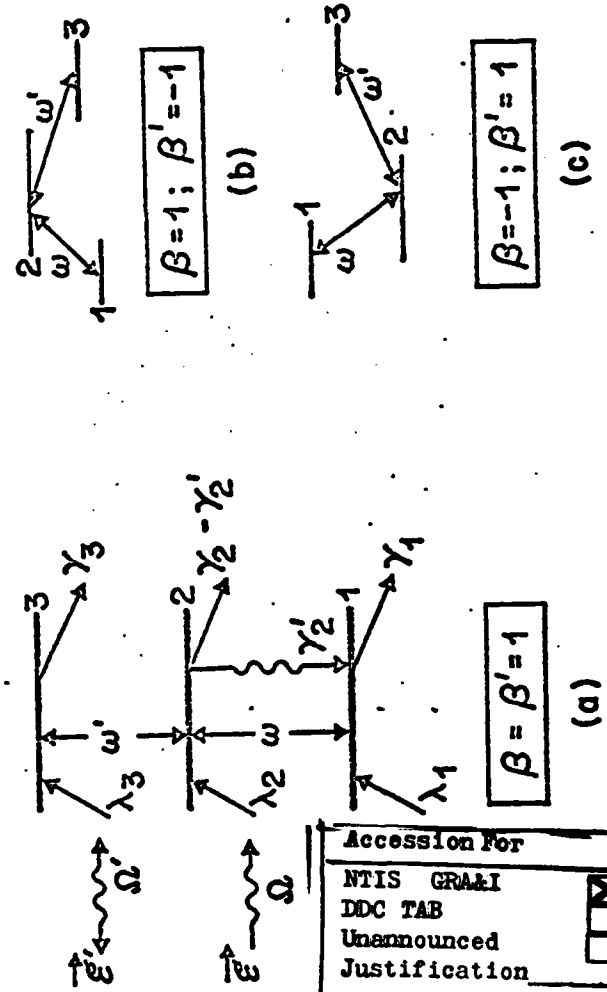


Fig. 1 Three-level systems: (a) upward cascade, (b) inverted V, (c) V.

and 2 - 3 transition (frequency ω'), respectively. The field propagation vectors are $k\hat{z}$ and $\epsilon k'\hat{z}$ ($k = \Omega/c$, $k' = \Omega'/c$) with ϵ equal to either +1 (copropagating) or - 1 (counterpropagating). Spontaneous emission between level 2 and 1 is allowed at rate γ_3'. The Rabi frequencies associated with the 1 - 2 and 2 - 3 transitions are denoted by χ and χ', respectively. I shall limit the discussion to the upward cascade (Fig. 1a) and take $\lambda_2 = \lambda_3 = 0$; $\lambda_1 = 0$, $\gamma_1 \neq 0$ λ_1/γ_1 = constant, to simulate level 1 being the ground state. The field at frequency Ω (pump) is of arbitrary strength and that at frequency Ω' (probe) is assumed to be weak.

The binary, elastic collisions between active atoms and ground state foreign gas perturbers are treated in the impact approximation.[2] Collisions are assumed to be "phase-interrupting" in their effect on level coherences (giving rise to broadening and shift parameters) and velocity-changing in their effect on population densities (i.e. collisions result in the relaxation of any velocity-selected population excited by the pump field). This rather simple collision model is generally valid for electronic transitions.

The pump field is detuned a fixed amount Δ from the 1-2 transition and the probe absorption is monitored as a function of its detuning Δ' from the 2-3 transition. If u is the most probable active atom speed, then two cases of interest are $|\Delta| \gg ku$., $|\Delta| < ku$.

$|\Delta| \gg ku$

If the pump detuning is equal to several Doppler widths, the only resonance in the absence of collisio occurs at $\Delta' = -\Delta + (k + \epsilon k')v_z$. When averaged over the active atom velocity distribution, the resulting line shape is a Voigt profile cent ed at $\Delta' = -\Delta$ with a width obtained from the convolution of a Lorentzian of of width (HWHM) $\gamma_3/2$ and a Gaussian of width $0.83(k + \epsilon k')u$, If $k \simeq k'$ and $\epsilon = -1$, this two-photon resonance can be very narrow.

With collisions present, a <u>new</u> resonance centered at $\Delta' = 0$ can result from a collisionally-aided radiative excitation[19] of level two <u>via</u> the reaction.

$$A_1 + P + \hbar\Omega \rightarrow A_2 + P$$

where A_i is the active-atom in state i and P is the perturber. The difference in energy between $\hbar\Omega$ and $\hbar\omega$ is now compensated by a corresponding change in the atoms' kinetic energy following a collision. With collisionally-aided excitation of level 2, probe absorption on the 2-3 transition centered at $\Delta' = 0$ can occur.

Thus, in the absence of collisions, there is only one resonance centered at $\Delta' = -\Delta$. In the presence of foreign gas perturbers, a new resonance appears at $\Delta' = 0$ which grows with increasing pressure. The width and shift of the $\Delta' = -\Delta$ resonance can be used to obtain the 1-3 broadening and shift coefficients, that of the $\Delta' = 0$ resonance to obtain the 2-3 broadening and shift coefficients. Moreover, the <u>amplitude</u> of the $\Delta' = 0$ resonance is proportional to the 1-2 broadening coefficient. Recent

experimental data[22] on $Na(3S_{1/2} \rightarrow 3P_{1/2} \rightarrow 4D_{3/2})$ perturbed by Ne is shown in Fig. 2. The effects of collisions for this large detuning case ($\Delta = -4.0$ ku, $k'/k = 1.0375$, $\epsilon = -1$) are clearly seen (the second narrow resonance centered at $\Delta' = 5.77$ku arises from ground state hyperfine structure).

$|\Delta| < ku$

The above type of experiment can provide total cross section data (total cross sections may be extracted from the broadening coefficients). However, to obtain information concerning differential cross sections, one must tune within the Doppler width. In this case, the pump laser selects a specific longitudinal velocity group having $v_z = \Delta/k$, leading to a resonance condition $\Delta' = -\Delta + (k + \epsilon k')v_z = \epsilon(k'/k)\Delta$. The resonance width is on the order of the natural widths of the transition levels, owing to the fact that only a small longitudinal velocity class of atoms is being used. The resonance is broadened and may even be split in strong pump fields, reflecting power broadening and the ac Stark effect, respectively. Probe absorption in the absence of collisions is shown in Fig. 3 for $k'/k = 0.4$. There is ac Stark splitting for counterpropagating waves in strong fields. For the case shown of complete branching to the ground state ($\gamma_2' = \gamma_2$), there is also some splitting for the copropagating case.

In the presence of collisions, the following interactions can occur:

$$A_1 + P + \hbar\Omega \rightarrow A_2(v_z' = \Delta/k) + P$$

$$A_2(v_z' = \Delta/k) + P \rightarrow A_2(v_z) + P$$

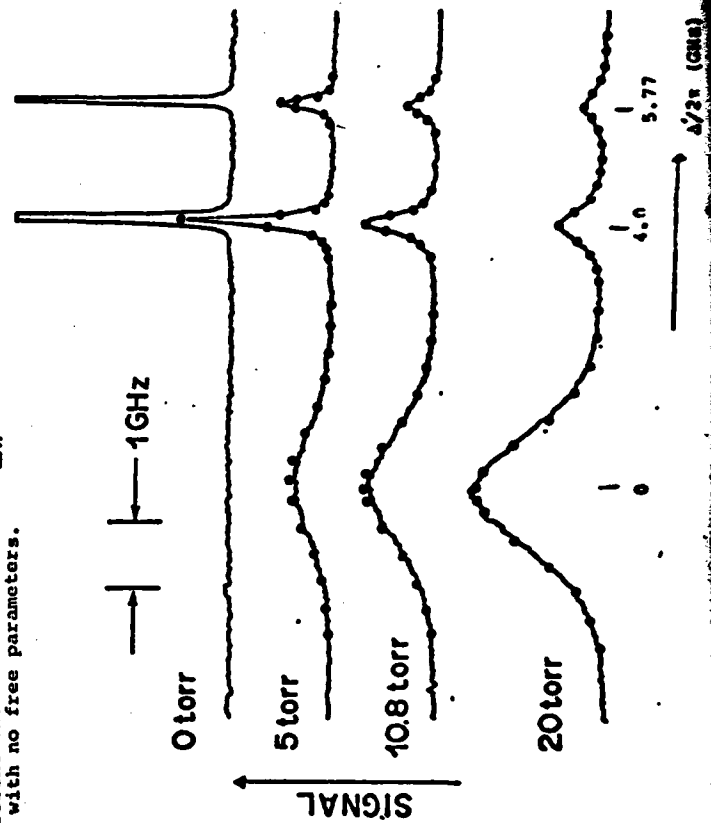
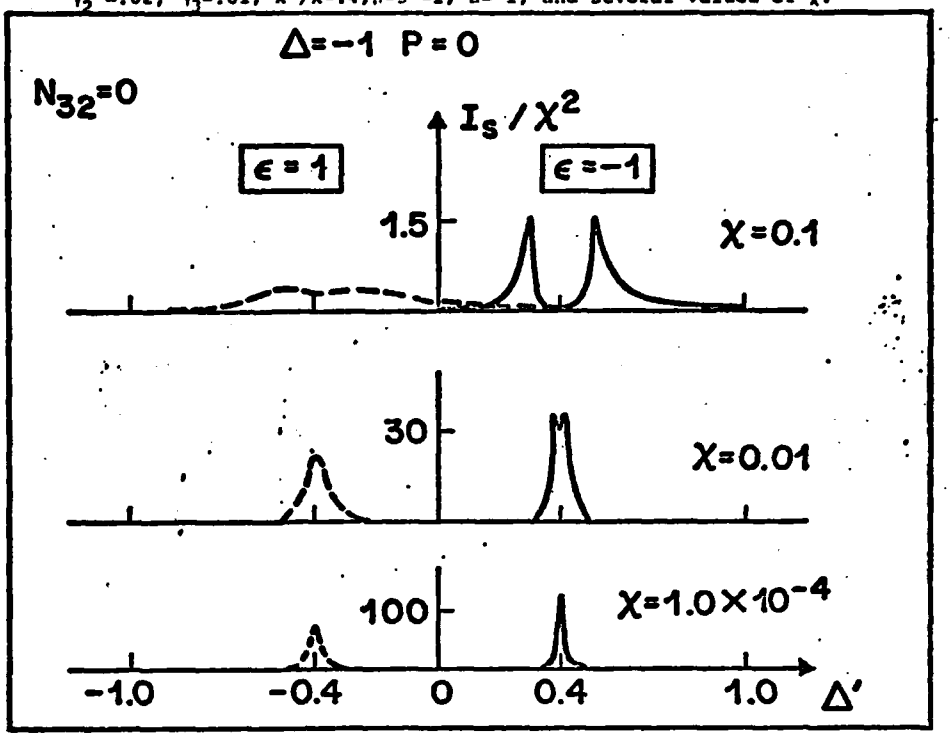


Fig. 2 Experimental excitation spectra for Na (3S→3P→4D) perturbed by various pressures of Ne for a pump detuning $\Delta/2\pi = -4.0$GHz. (Doppler width = 1.66ku/2π = 1.66 GHz.). Dots represent theoretical fit with no free parameters.

Fig. 3 Probe absorption I_s in the absence of collisions. I_s is normalized to χ^2, but is in arbitrary units. All frequencies are in units of ku, P is the pressure in Torr, and N_{32} (population difference of levels 3 and 2 in the absence of any applied fields) equals zero. The broken curve is for copropagating fields (ϵ=1) and the solid curve for counterpropagating ones (ϵ = -1). Profiles are drawn for γ_1=0, γ_2=.02, γ_2'=.02, γ_3=.01, k'/k=.4, β=β'=1, Δ=-1, and several values of χ.



Collisions result in an excitation of level 2 and a partial thermalization of the velocity distribution from the initial value $v_z' = \Delta/k$ selected by the pump field to values describing a thermal distribution. The degree of thermalization is determined by the number of collisions $n = \Gamma_2/\gamma_2$ (Γ_2 = collision rate) occurring within the lifetime of level 2 and the rms change in velocity per collision Δu. In addition, the structure of the velocity redistribution may be used to infer something about the interatomic potential giving rise to the scattering.

Theoretical probe absorption profiles for weak and strong pump fields are shown in Figs. 4 and 5, respectively, using the Kellson-Storer[21] collision kernel. One may note the gradual thermalization with increasing perturber pressure. In the strong field case both the integrated and peak probe absorption can increase with increasing pressure whereas, in the weak field case, the areas under the curves are constant.

Systematic experiments of this nature were recently carried out by Bréchignac et al[22] in Kr perturbed by rare gases and by, Liao et al[23] for Na perturbed by rare gases. The data for Na($3S_{1/2}$-$^3P_{1/2}$-$^4D_{3/2}$) perturbed by Ne is shown in Fig. 6 for a detuning Δ/ku = -1.6. The overall qualitative features are similar to those shown in Fig. 4 (for the three-level Na system chosen, k'/k = 1.0375 so that ac Stark splitting is suppressed). One can see the thermalization of the $^3P_{1/2}$ level of Na with increasing Ne pressure.

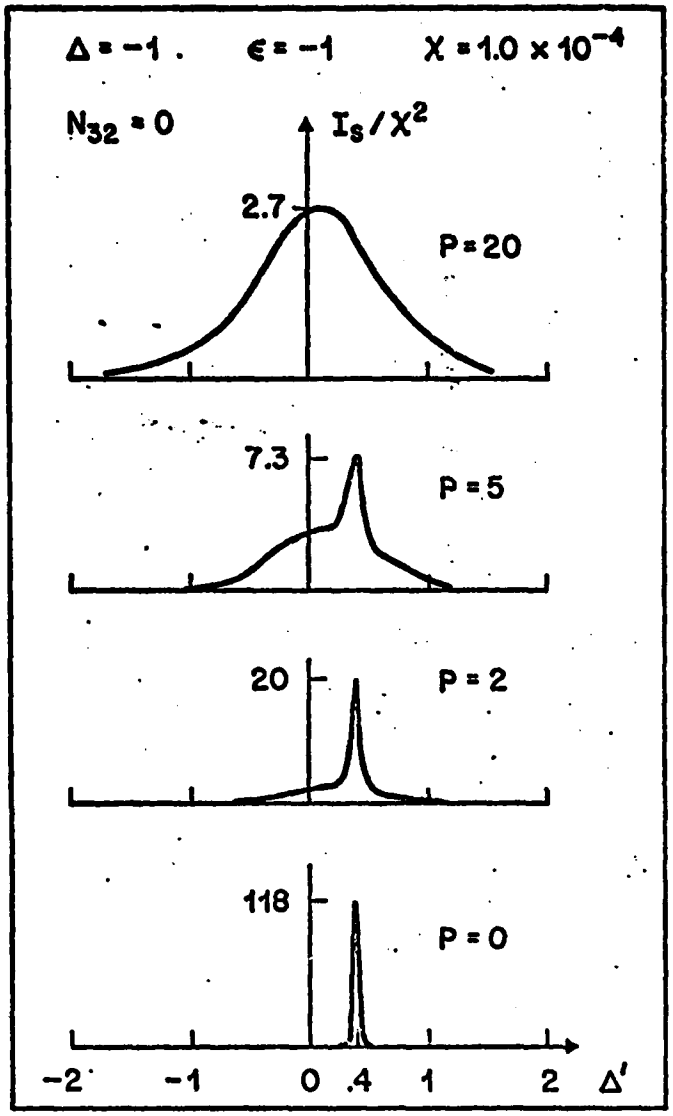


Fig. 4 Probe absorption in the weak pump field limit for various perturber pressures. Parameters not explicitly displayed are the same as in Fig. 3. Collision parameters (in units of ku) are as follows: phase-interrupting broadening rates Γ_{12}=.007P, Γ_{23}=.015P, Γ_{13}=.016P; velocity-changing collision rates Γ_1=.004P, Γ_2=.006P. A Keilson-Storer kernel with Δu=.66u is used to describe velocity-changing collisions.

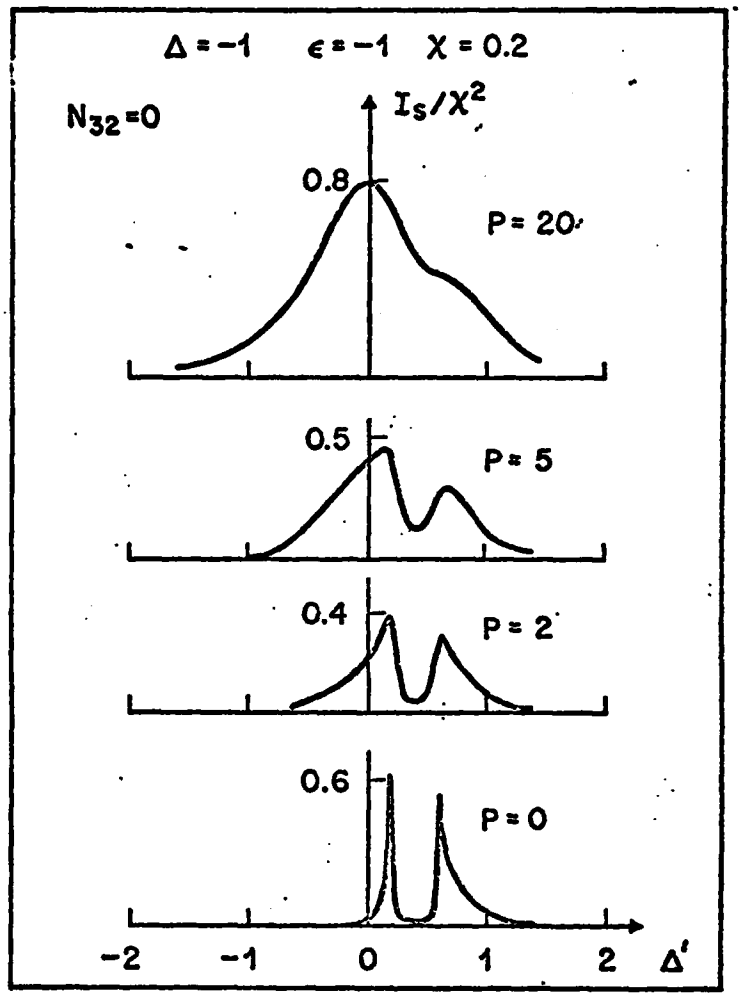


Fig. 5 Probe absorption for a strong pump field (χ=.2). Other parameters are as in Fig. 4.

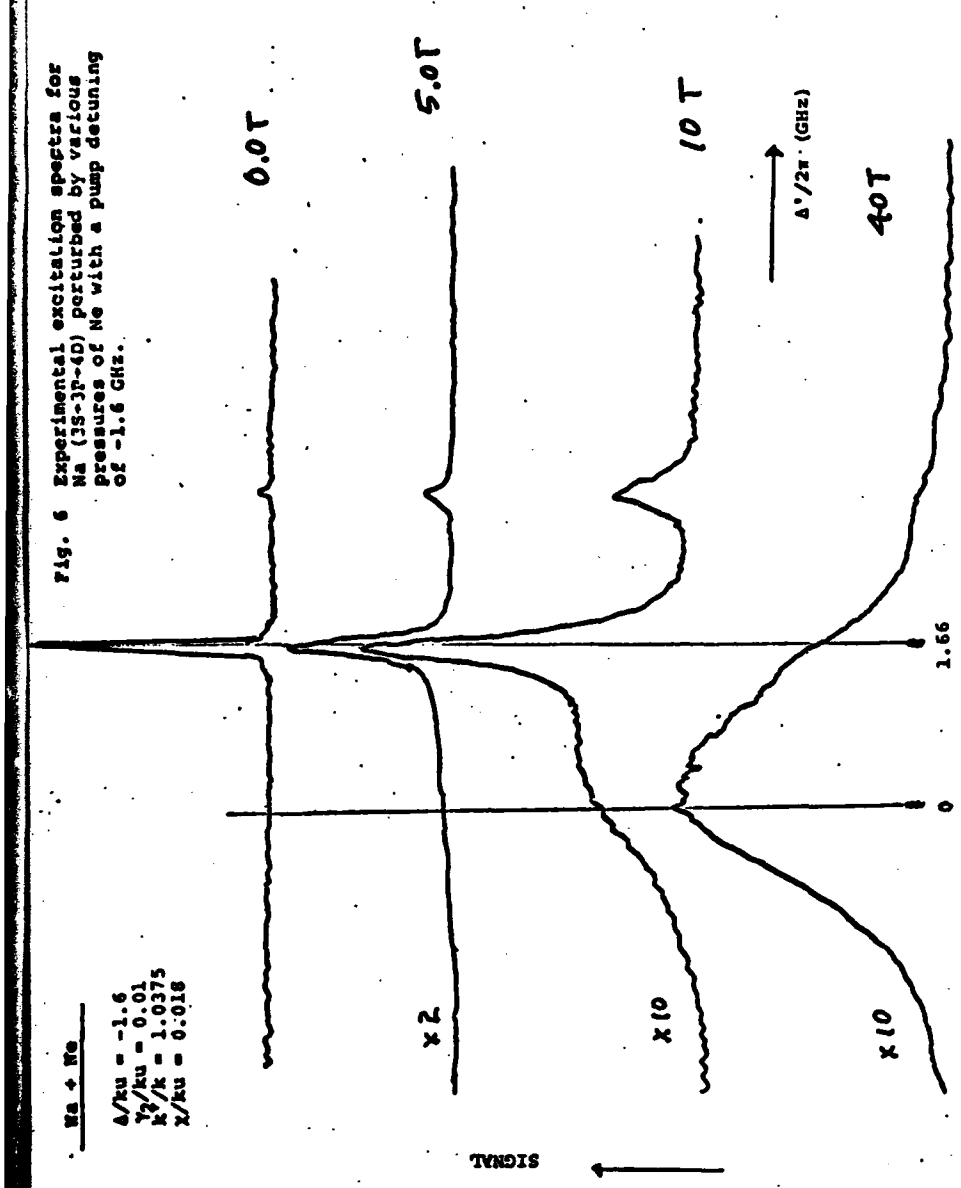


Fig. 6 Experimental excitation spectra for Na (3S-3P-4D) perturbed by various pressures of Ne with a pump detuning of -1.6 GHz.

The data of Liao et al[23] could also be used to test different collision kernels that are used to describe scattering in level 2. It was found that both the Keilson-Storer and classical Hard-Sphere kernels correctly characterized Na-He collisions, that the hard-sphere kernel was superior to Keilson-Storer for Na-Ne and Na-Kr collisions, and that neither kernel adequately described the entire profile for Na-Ne and Na-Kr collisions. These results imply that large-angle scattering of Na($3P_{1/2}$) with heavy foreign gases can not be characterized as totally hard-sphere in nature; it would not be surprising if some large-angle scattering could be attributed to attractive wells in the interatomic potentials. It appears to me that this type of experiment reflects an increased interest in both the experimental and theoretical[24] determination of atomic collision kernels.

Coherent Transients

It is also possible to carry out laser spectroscopic collisional studies using time resolved techniques. Some of these methods are particularly well suited to collisional studies. I shall mention two such types of experiments.

In time-delayed saturation spectroscopy, one uses a narrow band, pulsed laser to excite atoms having a given longitudinal velocity. A second laser, time delayed from the first, is then applied to the same or a coupled transition in order to monitor the velocity relaxation as a function of either time delay or perturber pressure. An advantage of this technique to steady-state

methods is that two-photon processes do not occur in the time-resolved experiment since the fields are applied at different times. Thus, the probe absorption occurs only from "stepwise" excitation, greatly simplifying the analysis. A limited number of experiments of this type have been performed.[25]

A second class of experiments which holds promise for collisional studies may be broadly characterized as photon echo experiments. In these experiments, a system is exposed to two or more pulses. The pulses lead to a dephasing and rephasing of atomic dipoles in the sample such that, at some time following the last applied pulse, the dipoles rephase and emit an "echo." Collisions disturb this dephasing-rephasing process and cause a decrease in echo amplitude. Thus, the echo amplitude can be used to monitor collisional processes in gases. This method is especially useful in determining whether collisions are "phase-interrupting" or "velocity-changing" in their effect on level coherences.[13, 14, 26]

By using standing waves as the excitation pulses, one excites higher-order harmonics in both populations and level coherences. The photon echoes following such excitation can reflect collisional effects on both population densities and level coherences.[27] Moreover, one can also observe population echoes as various population spatial harmonics rephase following the second pulse.[28] Studies of velocity-changing collisions on level populations can also be made using "stimulated" echoes,[29] which is simply a variation of the standing-wave echo method. Photon echo experiments offer an

interesting possibility for future collisional investigations.[28, 29]

Beam-Laser Experiment

Finally, I should like to mention the experiment of Phillips et al.[30] This experiment employed crossed atomic beams and a laser excitation-detection scheme. As in the steady-state experiment, a pump laser excites a particular velocity class of atoms to some intermediate state. A second laser, directed along the active atom-perturber relative velocity axis, is then scanned to probe a coupled transition. At each probe laser frequency, only those active atoms which have been scattered through a particular scattering angle θ (these atoms form a cone of angle θ about the laser axis) in the center-of-mass system resonantly interact with the probe. Thus, measuring the probe absorption is equivalent to measuring the differential scattering cross section. This method has high sensitivity and can be used for short-lived excited states; it was used to determine the differential cross section for $3P_{1/2} \rightarrow 3P_{3/2}$ fine structure state changing collisions in Na undergoing collisions with Ar perturbers.[30]

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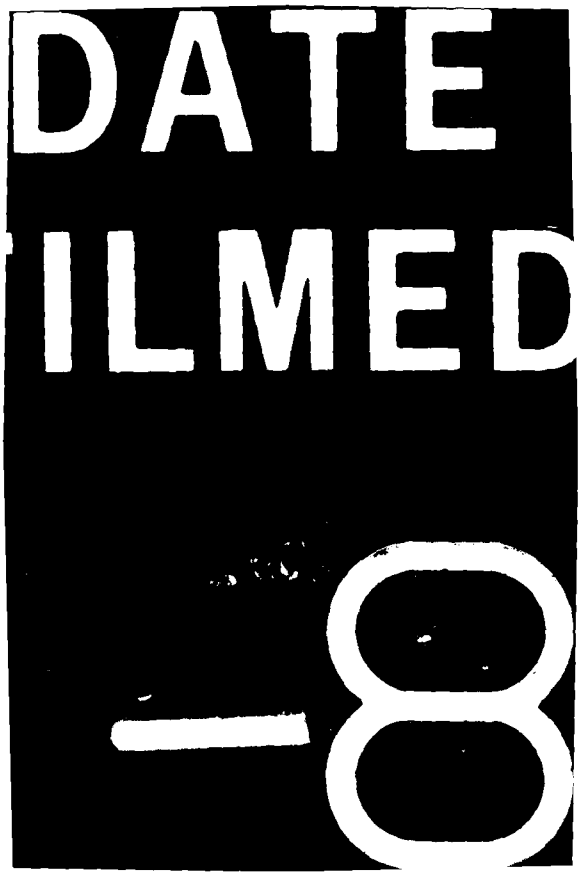
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